Removal of mercury(II) from aqueous media using eucalyptus bark: Kinetic and equilibrium studies

Ilhem Ghodbane, Oualid Hamdaoui *

Department of Process Engineering, Faculty of Engineering, University of Annaba, P.O. Box 12, 23000 Annaba, Algeria

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ABSTRACT

In this study, eucalyptus *camaldulensis* bark, a forest solid waste, is proposed as a novel material for the removal of mercury(II) from aqueous phase. The operating variables studied were sorbent dosage, ionic strength, stirring speed, temperature, solution pH, contact time, and initial metal concentration. Sorption experiments indicated that the sorption capacity was dependent on operating variables and the process was strongly pH-dependent. Kinetic measurements showed that the process was uniform and rapid. In order to investigate the mechanism of sorption, kinetic data were modeled using the pseudo-first-order and pseudo-second-order kinetic equations, and intraparticle diffusion model. Among the kinetic models studied, the pseudo-second-order equation was the best applicable model to describe the sorption process. Equilibrium isotherm data were analyzed using the Langmuir and the Freundlich isotherms. The Langmuir model yields a much better fit than the Freundlich model. Isotherms have also been used to obtain the thermodynamic parameters such as free energy, enthalpy, and entropy of sorption. The maximum sorption capacity was 33.11 mg g^{-1} at 20 °C and the negative value of free energy change indicated the spontaneous nature of sorption. These results demonstrate that eucalyptus bark is very effective in the removal of Hg(II) from aqueous solutions.

1. Introduction

Heavy metals are recognized as dangerous contaminants because of their high toxicity, accumulation, and retention in human body. Mercury, which is a remarkably toxic and non-biodegradable metal, can be generated by several sources, resulting in contamination of atmospheric and aquatic systems. The illness, which came to be known as Minamata disease, was caused by mercury poisoning as a result of eating contaminated fish [1]. Mercury has very high tendency for binding to proteins and it mainly affects the renal and nervous systems [2]. In humans, the initial symptoms include numbness of the lips and limbs. As the sickness progresses, permanent damage is done to the central nervous system, and the victim experiences visual constriction, loss of motor coordination, and, in the final stages prior to death, loss of memory, speech, hearing, and taste. In addition, mercury is easily absorbed through skin, respiratory, and gastrointestinal tissues. The European Union considers mercury as a priority and hazardous pollutant and defines a maximum permissible concentration of total mercury as low as 1 μg L^{-1} for drinking water and 5 μg L^{-1} for wastewater discharge [3,4]. Consequently, removal of mercury ions in water and wastewater is necessary and very important.

Several methods can be applied to remove mercury from aqueous solutions such as precipitation, electrolysis, ion exchange, adsorption, cementation, liquid membranes, and liquid–liquid extraction [5,6]. Adsorption has been shown to be the most promising technique for the removal of mercury from aqueous streams. However, the cost of adsorbents to be used is the most important restricted factor in view of applicability of adsorption process. Since commercially activated carbons are expensive, the search for alternative sorbents from cheaper and readily available materials that may be useful to reduce the pollutant content to the levels established by the legislation is a very attractive option. A number of agricultural waste and by-products have been studied in the literature for their capacity to remove mercury from aqueous solutions [7–11].

All mature eucalypts put on an annual layer of bark, which contributes to the increasing diameter of the stems. In some species the outermost layer dies and is annually deciduous either in long strips or in variably sized flakes. Due to the high number of eucalyptus trees in Algeria, massive amounts of barks (as waste) are disposed. Eucalyptus bark may be used as a potential sorbent for the removal of pollutants from aqueous phase. We used eucalyptus bark as a sorbent for the removing of Cd(II) ions [12] from aqueous solutions. It is observed that eucalyptus bark is an efficient

* Corresponding author. Tel.: +213 771598509; fax: +213 38876560.
E-mail address: ohamdaoui@yahoo.fr (O. Hamdaoui).

Nomenclature

b	Langmuir constant related to the free energy of sorption ($L\,mg^{-1}$)
b_M	Langmuir constant related to the free energy of sorption ($L\,mol^{-1}$)
c	the intercept in the intraprticle diffusion model ($mg\,g^{-1}$)
C_e	the equilibrium concentration of the solute in the bulk solution ($mg\,L^{-1}$)
C_0	the initial concentration of the solute in the bulk solution ($mg\,L^{-1}$)
h_1	initial sorption rate for the pseudo-first-order model ($mg\,g^{-1}\,min^{-1}$)
h_2	initial sorption rate for the pseudo-second-order model ($mg\,g^{-1}\,min^{-1}$)
k_{id}	the intraparticle diffusion rate constant ($mg\,g^{-1}\,min^{-1/2}$)
K_F	Freundlich constant indicative of the relative sorption capacity of the sorbent ($mg^{1-(1/n)}\,L^{1/n}\,g^{-1}$)
K_1	Lagergren pseudo-first order rate constant (min^{-1})
K_2	the pseudo-second order rate constant ($g\,mg^{-1}\,min^{-1}$)
m	sorbent mass (g)
n	Freundlich constant indicative of the intensity of the sorption
q	the amount of solute sorbed at any time t ($mg\,g^{-1}$)
q_e	the amount of solute sorbed per unit weight of sorbent at equilibrium ($mg\,g^{-1}$)
q_m	the maximum sorption capacity ($mg\,g^{-1}$)
R^2	coefficient of determination
R_g	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
R_L	dimensionless separation factor of Hall
t	time (min)
T	temperature (K)
V	solution volume (L)
$\Delta G°$	Gibb's free energy change ($kJ\,mol^{-1}$)
$\Delta H°$	enthalpy change ($kJ\,mol^{-1}$)
$\Delta S°$	entropy change ($J\,mol^{-1}\,K^{-1}$)

sorbent for the removal of these metal ions. Eucalyptus bark has also been successfully used for the removal of chromium anions from industrial waste and a sorption capacity of $45\,mg\,g^{-1}$ was found [13]. Eucalyptus barks were used for the adsorption of Cu(II), Cr(III), Cd(II), and Ni(II) [14] from aqueous phase. The adsorption capacities were 2.61, 0.71, 2.24, and $0.75\,mmol\,g^{-1}$ for Cu(II), Cr(III), Cd(II), and Ni(II), respectively. However, no work has been reported in the literature on the removal of mercury from aqueous media by eucalyptus bark.

The objectives of this study were to evaluate the sorption of mercury(II) ions by eucalyptus *camaldulensis* bark in batch process. The effect of operating conditions such as sorbent dosage, ionic strength, stirring speed, temperature, solution pH, contact time, and initial Hg(II) ion concentration were investigated on the sorption efficiency of mercury(II) ions. The sorption equilibrium data were analyzed using Langmuir and Freundlich models. In addition, thermodynamic parameters were determined for the sorption of mercury(II) ions to explain the process feasibility. In order to gain insight into the dynamics of the process, the mechanism controlling the sorption rate was also studied.

2. Materials and methods

2.1. Chemicals

Mercury solutions of desired concentration have been prepared by dissolving the appropriate amount of its chloride ($HgCl_2$, Sigma–Aldrich) in distilled water. All chemicals used in this study were of analytical grade.

2.2. Sorbent

The preparation of eucalyptus *camaldulensis* bark used as sorbent has been described in our previous study [12].

2.3. Equilibrium studies

Sorption experiments were carried out by adding a fixed amount of eucalyptus bark (2 g) into a number of 1 L sealed glass flasks containing a definite volume (500 mL in each case) of different initial concentrations ($25–300\,mg\,L^{-1}$) of mercury solution without changing pH. The flasks were placed in a thermostatic water bath in order to maintain a constant temperature (20, 30 or 40 °C) and stirring was provided at 400 rpm for 60 min to ensure equilibrium was reached. Samples of solutions were filtered through filter paper, and then the filtrates were analyzed for the remaining mercury concentration with atomic absorption spectrometry (PerkinElmer A310). The experiments were performed at pH 5, which resulted from dissolution of mercury chloride in distilled water without further adjustment. The amount of sorption at equilibrium, q_e ($mg\,g^{-1}$), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 and C_e ($mg\,L^{-1}$) are the initial and equilibrium liquid-phase concentrations of metal, respectively. V (L) is the volume of the solution and m (g) is the mass of the dry sorbent used.

All experiments were conducted in triplicate and the mean values were reported. The maximum standard deviation obtained for triplicate measurements of the sorbed amount was ±2%.

2.4. Kinetic studies

The initial concentration of mercury solution was $100\,mg\,L^{-1}$ for all experiments, except for those carried out to examine the effect of the initial concentration of mercury. For mercury removal kinetic experiments, the batch method was used because of its simplicity: 2 g of sorbent was contacted with 500 mL of metal solution in a sealed flask of 1 L agitated vigorously by a mechanic stirrer using a water bath maintained at a constant temperature. The stirring speed was kept constant at 400 rpm, except for experiments carried out to investigate the effect of stirring speed. At predetermined intervals of time, samples of the mixture was withdrawn at suitable time intervals, filtered through a paper filter, and analyzed by atomic absorption spectrometry (PerkinElmer A310) for the concentration of mercury.

The experiments were performed at the pH that resulted from solving the metal in water (around 5) without further adjustment, except for those conducted to examine the effect of solution pH.

To study the effect of solution pH on mercury sorption, 2 g of eucalyptus bark was agitated with 500 mL of mercury solution of metal concentration $100\,mg\,L^{-1}$ at 20 °C. The experiment was conducted at different pH values ranging from 2 to 10. The solution pH was adjusted using 0.1N H_2SO_4 or NaOH aqueous solutions. Agitation was provided for 60 min contact time which is sufficient to reach equilibrium with a constant agitation speed of 400 rpm.
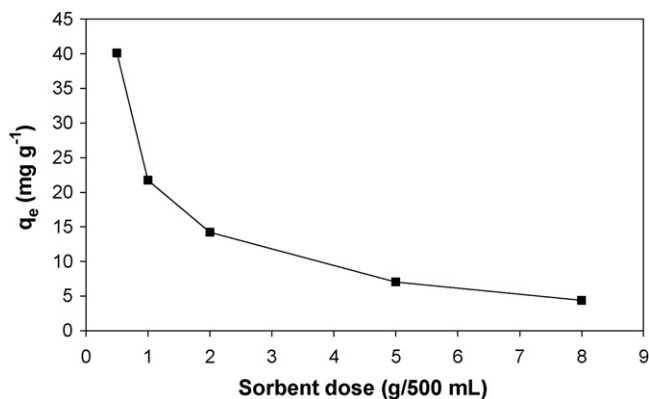
Fig. 1. Effect of sorbent dosage on the sorption of mercury by eucalyptus bark (conditions: metal concentration = 100 mg L^{-1}; contact time = 60 min; stirring speed = 400 rpm; T = 20 °C; pH 5).

Fig. 2. Effect of salt (Na$_2$SO$_4$) concentration on the sorption of mercury by eucalyptus bark (conditions: metal concentration = 100 mg L^{-1}; sorbent dosage = 2 g (500 mL)$^{-1}$; contact time = 60 min; stirring speed = 400 rpm; T = 20 °C; pH 5).

The influence of ionic strength on the sorption of mercury by eucalyptus bark was studied with a constant initial concentration of 100 mg L^{-1}, sorbent mass of 2 g, solution volume of 500 mL, and temperature of 20 °C. The ionic strength of the mercury solution was modified using different dosages of Na$_2$SO$_4$ (0.5–20 g (500 mL)$^{-1}$).

In all the experiments in which the effect of stirring speed was studied, the initial mercury concentration, sorbent mass, and solution temperature were 100 mg L^{-1}, 2 g, and 20 °C, respectively. The stirring speed was varied from 0 (without stirring) to 1200 rpm.

Each run of the experiments was replicated at least two times and the mean values were reported. The maximum standard deviation obtained for duplicate or triplicate measurements of the sorbed amount was ±2%.

3. Results and discussion

3.1. Effect of operating conditions

The influence of several operating conditions such as sorbent dosage, ionic strength, stirring speed, temperature, and solution pH on the sorption capacity was investigated.

3.1.1. Effect of sorbent dosage

The sorption of mercury by eucalyptus bark sorbent was studied by changing the quantity of sorbent in the test solution while maintaining the initial metal ions concentration (100 mg L^{-1}), temperature (20 °C), stirring speed (400 rpm), contact time (60 min), and pH (pH 5) constant. The effect of sorbent dosage on the amount of mercury sorbed at equilibrium is shown in Fig. 1. The amount of metal sorbed at equilibrium decreases from 40.12 to 4.39 mg g^{-1} with an increase of sorbent dosage between 0.5 and 8 g (500 mL)$^{-1}$. The increase in sorbent dose at constant metal concentration and volume will lead to unsaturation of sorption sites through the sorption process. At higher eucalyptus bark to metal concentration ratios, there is a superficial sorption onto the sorbent surface that produces a lower metal concentration in the solution than when the sorbent to metal concentration ratio is lower. This is because a fixed mass of eucalyptus bark can only sorb a certain amount of mercury. Therefore, the higher the sorbent dosage is, the larger is the volume of effluent that a fixed mass of eucalyptus bark can purify. The decrease in the amount of mercury sorbed with increasing sorbent dosage is due to the split in the flux or the concentration gradient between mercury concentrations in the solution and on the sorbent surface. Additionally, this decrease may be attributed to overlapping or aggregation of sorption sites resulting in decrease in total
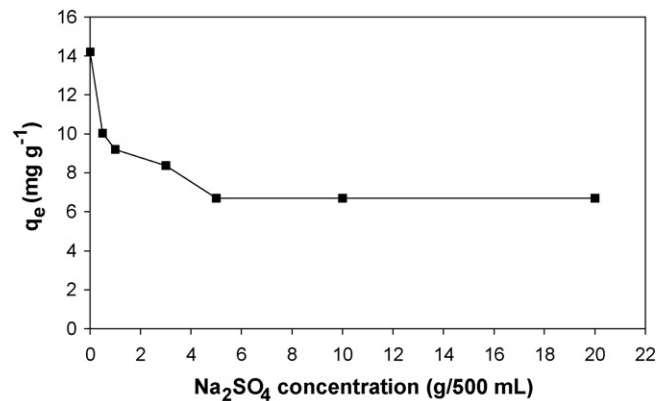
sorbent surface area available to metal ions and an increase in diffusion path length. On the other hand, an increase in the eucalyptus bark dosage from 0.5 to 8 g (500 mL)$^{-1}$ increases the percentage of metal removal from aqueous solution from 39.8 to 69.9%. This may be attributed to increased sorbent surface area and availability of more sorption sites resulting from the increased dose of the sorbent.

3.1.2. Effect of ionic strength

A series of experiments were carried out using various concentrations of salt (Na$_2$SO$_4$). The results reported in Fig. 2 indicated that the amount sorbed at equilibrium decreased by increasing the salt concentration and reached a constant value after 5 g (500 mL)$^{-1}$. This behavior could be attributed to the competitive effect between mercury ions and cations from the salt (Na$^+$) for the sites available for the sorption process. Additionally, salt screens the electrostatic interaction between sorbent and sorbate and the great ionic strength influences on the activity coefficient of mercury, which should decrease the sorbed amount with increase of salt concentration.

3.1.3. Effect of stirring speed

Fig. 3 shows the sorption of mercury by eucalyptus bark sorbent at different stirring speed, ranging from 0 (without stirring) to 1200 rpm using a contact time of 60 min. The sorption capacity obtained without stirring is 7.52 mg g^{-1}. The amount of metal per unit mass of sorbent at equilibrium increased from 8.36 to 14.21 mg g^{-1} with increasing stirring speed from 150 to
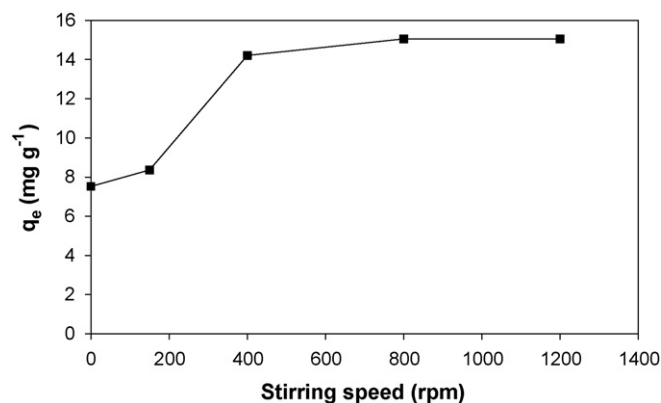
Fig. 3. Effect of stirring speed on the sorption of mercury by eucalyptus bark (conditions: metal concentration = 100 mg L^{-1}; sorbent dosage = 2 g (500 mL)$^{-1}$; contact time = 60 min; T = 20 °C; pH 5).
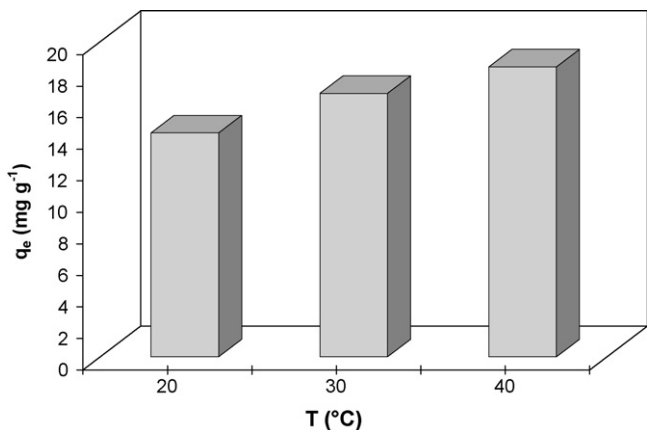
Fig. 4. Effect of temperature on the sorption of mercury by eucalyptus bark (conditions: metal concentration = 100 mg L^{-1}; sorbent dosage = 2 g (500 mL)$^{-1}$; contact time = 60 min; stirring speed = 400 rpm; pH 5).

400 rpm. This can be explained by the fact that increasing stirring speed reduced the film boundary layer surrounding particles, thus increasing the external film transfer coefficient, and hence the sorption capacity. The change in sorption capacity was insignificant compared to the dissipated energy when the stirring speed increased from 400 to 1200 rpm.

3.1.4. Effect of temperature

Fig. 4 shows the amount of mercury sorbed at equilibrium versus the temperature. It was found that the sorption capacity increased with the increase in temperature, indicating the endothermic nature of the process. The enhancement in the sorption capacity might be due to the interaction between sorbate ions and sorbent, creation of some new sorption sites or the increased rate of intraparticle diffusion of mercury ions into the pores of the sorbent at higher temperatures. The amount of mercury sorbed at equilibrium increased from 14.21 to 18.39 mg g^{-1} with the increasing of temperature from 20 to 40 °C, respectively.

3.1.5. Effect of pH

The effect of solution pH on the amount of mercury sorbed was studied by varying the initial pH under constant process parameters at equilibrium conditions. From Fig. 5, it was observed that the sorption was strongly pH-dependent. The maximum sorption capacity takes place at pH 8 and beyond this pH sorbent attains the same maximum value. The equilibrium sorption capacity was minimum at pH 2 (5.01 mg g^{-1}) and increased up to pH 6 (16.04 mg g^{-1}), reached maximum (20.06 mg g^{-1}) over the pH 8–10. The variation
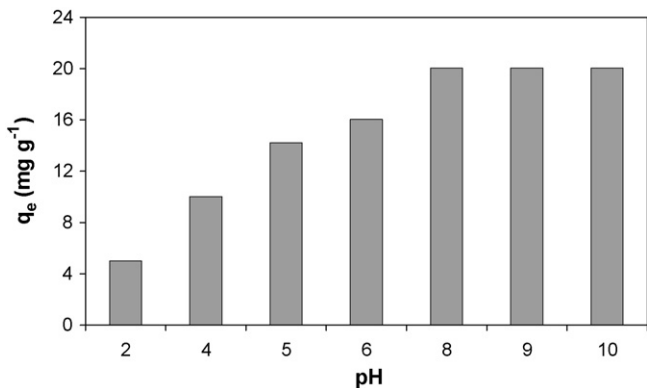
Fig. 5. Effect of pH on the sorption of mercury by eucalyptus bark (conditions: metal concentration = 100 mg L^{-1}; sorbent dosage = 2 g (500 mL)$^{-1}$; contact time = 60 min; stirring speed = 400 rpm; T = 20 °C).
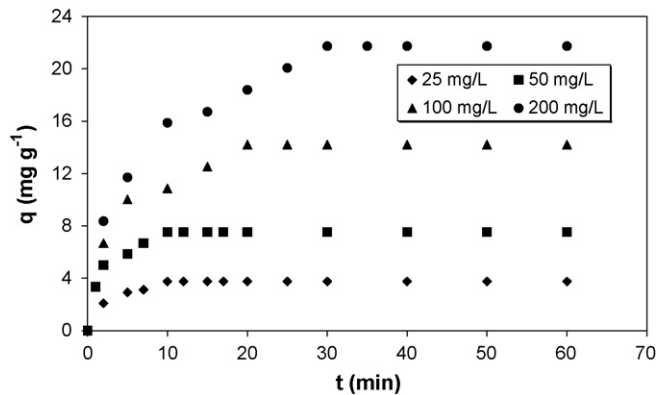
Fig. 6. Dynamics of mercury uptake by eucalyptus for various initial metal concentrations (conditions: sorbent dosage = 2 g (500 mL)$^{-1}$; stirring speed = 400 rpm; T = 20 °C; pH 5).

in the removal of mercury by eucalyptus bark with respect to pH can be elucidated by considering the surface charge of the sorbent materials and the speciation of mercury(II). At low pH values (2–4), the number of negatively charged surface sites decreased and the number of positively charged sites increased, which did not favor the sorption of positively charged metal ions (Hg^{2+} and Hg(OH)$^+$) due to electrostatic repulsion. Additionally, lower sorption of mercury at acidic pH is due to the presence of excess H$^+$ ions competing with metal ions for the sorption sites. The increase in Hg(II) sorption in the pH range 2–6 is due, in addition to the less competition from protons to reaction sites, to an increase in concentration of Hg(OH)$^+$ species, and to the fact that the solution pH influences the sorbent surface charge. The PZC of eucalyptus bark is 5.32. The surface charge of the eucalyptus bark is positive at pH < 5.32, is neutral at pH 5.32, and is negative at pH > 5.32. At high pH values (6–10), greater than 5.32, eucalyptus bark becomes negatively charged and the Hg(II) species are still present mainly as Hg(OH)$^+$ and Hg(OH)$_2$ at pH 6 and as Hg(OH)$_2$ at pH 8–10. The increase in Hg(II) uptake for very high pH values (8–10) is due to the retention of Hg(OH)$_2$, the dominant species of Hg(II) at these pHs, by the sorbent.

3.1.6. Effect of contact time and initial concentration

The sorption data for the uptake of mercury versus contact time at different initial concentrations ranging from 25 to 200 mg L^{-1} are presented in Fig. 6. It can be observed that the sorption capacity increased with time and, at some point in time, reached a constant value where no more metal was removed from the solution. At this point, the amount of mercury being sorbed by the sorbent was in a state of dynamic equilibrium with the amount of mercury desorbed from the sorbent. The contact time needed for mercury solutions with initial concentrations of 25 and 50 mg L^{-1} to reach equilibrium was 10 min. For mercury solution with initial concentrations of 100 and 200 mg L^{-1}, equilibrium time of 20 and 30 min, respectively, was required. This is due to the fact that sorption sites took up the available metal ions more quickly at low concentration, but metal needed to diffuse to the inner sites of the sorbent for high concentration. The kinetic results also showed that the sorption process was uniform with time and can be considered very fast. Additionally, the curves of contact time are single, smooth, and continuous leading to equilibrium. These curves indicate the possible monolayer coverage of metal on the surface of eucalyptus bark.

From Fig. 6, it was observed that the mercury removal varied with varying initial metal concentration. It was noticed that an increase in initial metal concentration leads to an increase in the sorption capacity of mercury by eucalyptus bark. Equilibrium uptake increased with the increase of initial metal concentration

at the range of experimental concentration. This is a result of the increase in the driving force the concentration gradient, as an increase in the initial mercury concentrations. The removal of mercury sorbed after equilibrium was 3.76, 7.52, 14.21, and 21.73 mg g^{-1}, respectively, at an initial concentrations of 25, 50, 100, 200 mg L^{-1}. The initial rate of sorption was greater for higher initial mercury concentration, because the resistance to the metal uptake decreased as the mass transfer driving force increased. It is also noticed that an increase in the initial mercury concentration leads to a decrease in the metal removal. This effect can be explained as follows: at low metal/sorbent ratios, there are a number of sorption sites in eucalyptus bark structure. As the metal/sorbent ratio increases, sorption sites are saturated, resulting in decreases in the sorption efficiency.

3.2. Sorption kinetics

In order to investigate the kinetics of mercury sorption by eucalyptus bark, the Lagergren pseudo-first-order model [15] and the Ho's linear form [16,17] of the pseudo-second-order model, developed by Blanchard [18], were used.

A simple kinetic analysis of sorption can be performed with a pseudo-first-order equation as suggested by Lagergren [15]

$$\frac{dq}{dt} = K_1(q_e - q) \tag{2}$$

where K_1 (min^{-1}) is the rate constant of the pseudo-first-order sorption, q_e (mg g^{-1}) is the amount of mercury sorbed on the sorbent surface at equilibrium, and q (mg g^{-1}) is the amount of mercury sorbed at any time t (min). Eq. (2) above can be integrated to the following form by applying the boundary conditions $q = 0$ at $t = 0$

$$\ln(q_e - q) = \ln q_e - K_1 t \tag{3}$$

This rate expression is known as the Lagergren pseudo-first-order equation.

Since $q = 0$ at $t = 0$, the initial rate of sorption can be calculated from Eq. (4) as follows

$$h_1 = K_1 q_e \tag{4}$$

The values of K_1 and q_e can be determined by the slope of linear plots of $\ln(q_e - q)$ versus t (Fig. 7). The parameters of the pseudo-first-order model are summarized in Table 1. The values of determination coefficient for the plots were in the range 0.9481–0.9863. However, although the coefficient of determination value is reasonably high, the calculated sorption capacity values obtained from this kinetic model do not give reasonable values compared with experimental sorption capacity. This finding suggested that the sorption process does not follow the pseudo-first-order sorption rate expression of Lagergren.
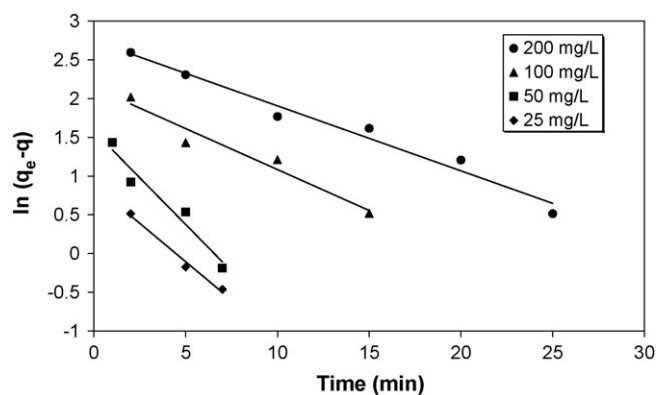
An expression of the pseudo-second-order rate based on the solid capacity has been presented by Blanchard [18]

$$\frac{dq}{dt} = K_2(q_e - q)^2 \tag{5}$$

Fig. 7. Lagergren plots for mercury sorption by eucalyptus bark at different initial metal concentrations (conditions: sorbent dosage = 2 g (500 mL)$^{-1}$; stirring speed = 400 rpm; T = 20 °C; pH 5).
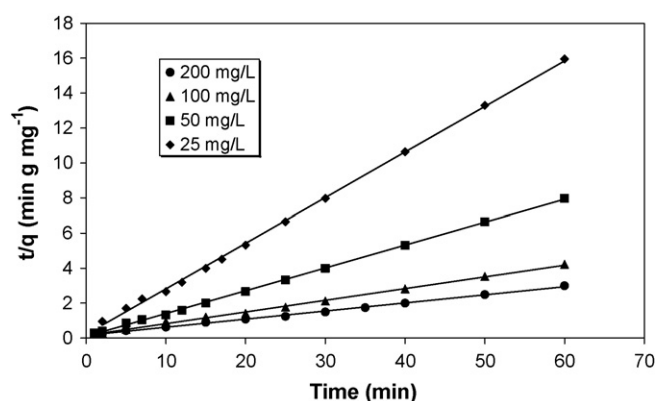
Fig. 8. Pseudo-second-order kinetics of mercury sorption by eucalyptus bark at different initial metal concentrations (conditions: sorbent dosage = 2 g (500 mL)$^{-1}$; stirring speed = 400 rpm; T = 20 °C; pH 5).

where K_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}), q_e is the amount of metal sorbed at equilibrium (mg g^{-1}), and q is the amount of metal ions on the surface of the sorbent at any time t (mg g^{-1}).

Integrating Eq. (5), considering that $q = 0$ when $t = 0$ and that $q = q$ when $t = t$, results in the expression [16,17].

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

The initial sorption rate h (mg g^{-1} min^{-1}) is given by the following equation

$$h_2 = K_2 q_e^2 \tag{7}$$

By plotting t/q versus t (Fig. 8), q_e and K_2 can be determined from slope and intercept. As mentioned above, the curve fitting plots of $\ln(q_e - q)$ versus t does not show good results, while the plots of t/q versus t give a straight line for all the initial metal concentrations studied as showed in Fig. 8, confirming the applicability of
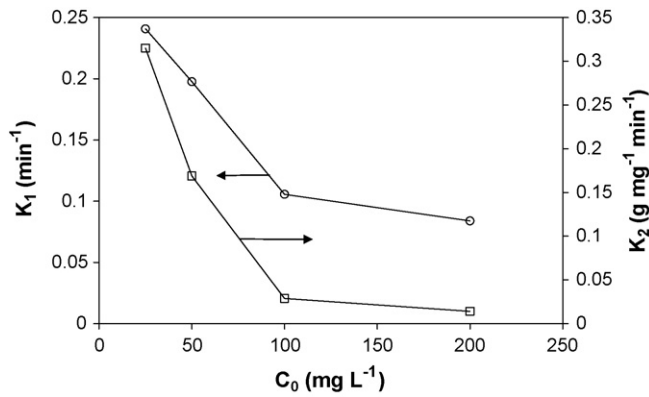
Table 1
Comparison of the pseudo-first-order (K_1) and pseudo-second-order (K_2) parameters for the sorption of mercury at various initial concentrations (conditions: sorbent dosage = 4 g L^{-1}; stirring speed = 400 rpm; T = 20 °C; pH 5)

C_0 (mg L^{-1})	$q_{e\,exp}$ (mg g^{-1})	Pseudo-first-order model				Pseudo-second-order model			
		K_1 (min^{-1})	$q_{e\,calc}$ (mg g^{-1})	h_1 (mg g^{-1} min^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	$q_{e\,calc}$ (mg g^{-1})	h_2 (mg g^{-1} min^{-1})	R^2
25	3.76	24.08×10^{-2}	4.85	1.17	0.9863	31.51×10^{-2}	3.84	1.21	0.9991
50	7.52	19.76×10^{-2}	2.41	0.48	0.9481	16.88×10^{-2}	7.66	1.29	0.9994
100	14.21	10.56×10^{-2}	8.49	0.90	0.9497	2.88×10^{-2}	14.95	0.43	0.9981
200	21.73	8.39×10^{-2}	15.53	1.30	0.9739	1.41×10^{-2}	21.55	0.30	0.9979

Fig. 9. Evolution of K_1 and K_2 versus initial mercury concentration.

the pseudo-second-order equation. The parameters of the pseudo-second-order sorption kinetic model are tabulated in Table 1. The determination coefficient values of the pseudo-second-order model exceeded 0.99 and the calculated sorption capacity values determined from pseudo-second-order model were more consistent with the experimental values of sorption capacity. Therefore, the pseudo-second-order model better represented the sorption kinetics and thus supports the assumption behind the model. This suggests that the overall rate of the mercury sorption process appeared to be controlled by chemical process.

In order to differentiate the kinetic constants obtained for the two models, the obtained K_1 and K_2 values were plotted against the initial metal concentration (Fig. 9). It was observed that the values of rate constants decrease with increasing the initial concentration of mercury from 25 to 200 mg L^{-1}. A larger rate constant implies that it will take shorter time for the sorption system to reach the same fractional uptake. Therefore, the trend that K_1 and K_2 decrease with increasing C_0 in the range 25–200 mg L^{-1} only reveals the fact that it is faster for a sorption system with a lower initial concentration to reach a specific fractional uptake. Additionally, it was noticed that there was no linear relationship between the rate constants and initial metal concentration. This reflects the different mathematical forms of Eqs. (3) and (6).

3.3. Sorption equilibrium

In order to optimize the design of a sorption system to remove metal ions from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Experimental data were fitted to the well-known and widely applied isotherm models of Langmuir and Freundlich. The linear equations are given below:

$$\text{Langmuir}: \frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b} \tag{8}$$

$$\text{Freundlich}: \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{9}$$

where C_e (mg L^{-1}) and q_e (mg g^{-1}) are the liquid phase concentration and solid phase concentration of sorbate at equilibrium, respectively; b (L mg^{-1}) is the Langmuir isotherm constant; q_m (mg g^{-1}) is the maximum sorption capacity of Langmuir; K_F is the Freundlich constant (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}), and n is the heterogeneity factor.

The sorption data obtained at 20, 30, and 40 °C were analyzed according to the linear form of the Langmuir isotherm (Eq. (8)). The plots of C_e/q_e versus C_e give a straight line of slope $1/q_m$ and intercept $1/bq_m$ (Fig. 10a). The Langmuir constants are reported in Table 2. The isotherm was found to be linear over the entire
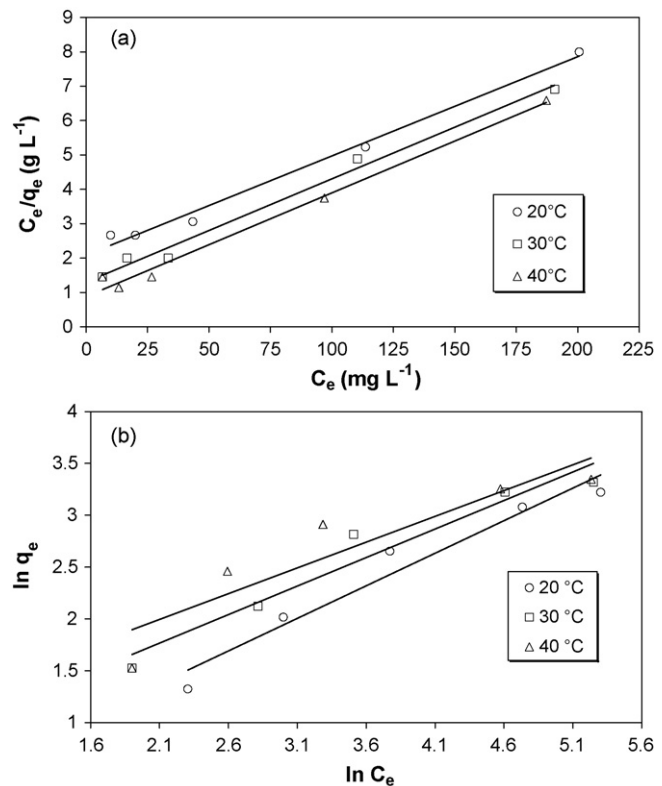

Fig. 10. Sorption isotherms for mercury by eucalyptus bark at 20, 30, and 40 °C: (a) Langmuir isotherm and (b) Freundlich isotherm (conditions: sorbent dosage = 2g (500 mL)$^{-1}$; agitation speed = 400 rpm; pH 5).

concentration range studied and for the three temperatures with a good linear regression coefficient, showing that data correctly fit the Langmuir relation. The monolayer saturation capacity, q_m, was found to be 33.11, 33.22, and 34.60 mg g^{-1} at 20, 30, and 40 °C, respectively. The fact that Langmuir isotherm fits the experimental data very well confirms the monolayer coverage of metal ions onto particles and also the homogenous distribution of active sites on the material, since the Langmuir equation assumes that the surface is homogenous.

Examination of the linear Freundlich isotherm plots (Fig. 10b) suggested that the Langmuir model yielded a much better fit than the Freundlich model. Table 2 shows the Freundlich constants and the regression coefficients. The values of the regression coefficient were much lower than the Langmuir isotherm values. The values of Freundlich exponent n in the range 1–10 indicate the favorable sorption. However, based on the regression coefficient values, the linear form of the Langmuir isotherm appears to produce a reasonable model.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by Eq. (10) [19].

$$R_L = \frac{1}{1 + bC_0} \tag{10}$$

Table 2
Parameters of the Langmuir and Freundlich isotherm models

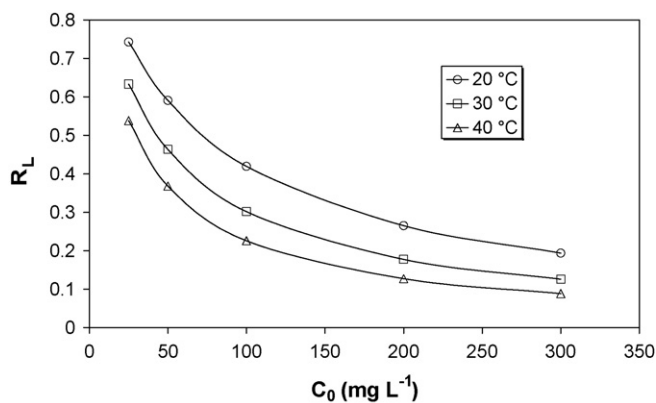| T (°C)	Langmuir			Freundlich		
	q_m (mg g^{-1})	b (L mg^{-1}) $\times 10^3$	R^2	K_F (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1})	n	R^2
20	33.11	13.86	0.9907	1.06	1.59	0.9517
30	33.22	23.17	0.9900	1.84	1.82	0.9429
40	34.60	34.32	0.9898	2.59	2.01	0.8483

Fig. 11. Separation factor for the uptake of mercury by eucalyptus bark at 20, 30, and 40 °C.

where b is the Langmuir constant and C_0 is the initial concentration of the sorbate in solution.

The values of R_L indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The calculated R_L values versus initial mercury concentration were represented in Fig. 11. From this figure, it was observed that sorption was found to be more favorable at higher concentrations. Also the value of R_L in the range of 0–1 at all initial metal concentrations and the three studied temperatures confirms the favorable uptake of mercury process.

In the sense of the sorption thermodynamics, change in free energy (ΔG°) of the removal of mercury by eucalyptus bark can be calculated in a way such that

$$\Delta G^\circ = -R_g T \ln b_M \tag{11}$$

where T (K) is the absolute temperature, R_g (kJ mol^{-1} K^{-1}) is the gas constant, and b_M (L mol^{-1}) is the Langmuir equilibrium constant.

It is known that ΔG° is the function of change in enthalpy of sorption (ΔH°) as well as change in standard entropy (ΔS°):

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{12}$$

If Eq. (12) is inserted into Eq. (11), it becomes

$$\ln b_M = \frac{\Delta S^\circ}{R_g} - \frac{\Delta H^\circ}{RT} \tag{13}$$

It appears from Eq. (13) that both ΔS° and ΔH° of sorption can be determined from the plot of $\ln b_M$ to $1/T$ (Fig. 12). The thermodynamic parameters are shown in Table 3. The negative values of ΔG° indicate that the mercury sorption process could occur spontaneously. ΔG° decreases with an increase in temperature, indicating that sorption of mercury by eucalyptus bark is spontaneous and spontaneity increases with an increase in temperature. The value
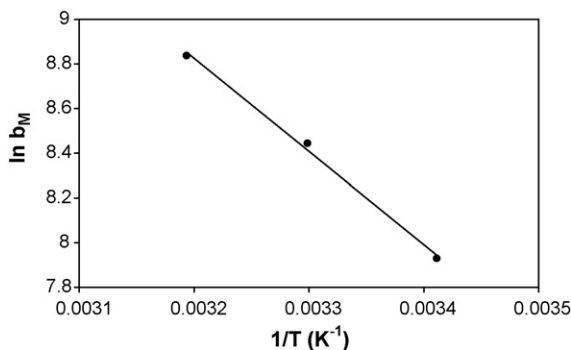

Fig. 12. Plot of $\ln b_M$ versus $1/T$ for the determination of thermodynamic parameters.

Table 3
Thermodynamic parameters for the sorption of mercury by eucalyptus bark

T (°C)	20	30	40
ΔG° (kJ mol^{-1})	−19.32	−21.27	−23.00
ΔH° (kJ mol^{-1})	34.64		
ΔS° (J mol^{-1} K^{-1})	184.22		

of ΔH° was estimated as 34.64 kJ mol^{-1} and 184.22 J mol^{-1} K^{-1} for ΔS°. Basically, the heat evolved during physical sorption is of the same order of magnitude as the heat of condensation, i.e., 2.1–20.9 kJ mol^{-1} [20], while the heat of chemisorption generally falls into a range of 80–200 kJ mol^{-1} [21]. Therefore, it seems that mercury sorption by eucalyptus bark would be attributed to a physicochemical sorption process rather than a pure physical or chemical sorption process. The positive value of ΔH° indicates that mercury sorption is an endothermic process. The low value of ΔS° may imply that no remarkable change in entropy occurred during the sorption of mercury by the material. In addition, the positive value of ΔS° reflects the increased randomness at the solid–solution interface during sorption, and it also indicates an affinity of the sorbent toward mercury. Normally, adsorption of gases leads to a decrease in entropy due to orderly arrangement of the gas molecules on a solid surface. However, the same may not be true for the complicated system of sorption from solution onto eucalyptus bark.

3.4. Sorption mechanism

Since neither the pseudo-first-order nor the pseudo-second-order models can identify the diffusion mechanism, the kinetic results were analyzed by the intraparticle diffusion model. Since the particles are vigorously agitated during the sorption period, it is assumed that the rate is not limited by mass transfer from the bulk liquid to the particle external surface. The rate-limiting step may be film or intraparticle diffusion. The Weber and Morris [22] intraparticle diffusion model is expressed as:

$$q = k_{id}t^{1/2} + c \tag{14}$$

where q (mg g^{-1}) is the amount of mercury sorbed at time t, c (mg g^{-1}) the intercept, and k_{id} (mg g^{-1} min$^{-1/2}$) is the intraparticle diffusion rate constant.

Fig. 13 shows the amount of metal sorbed versus $t^{1/2}$ for intraparticle transport of mercury by eucalyptus bark at different initial metal concentrations. The k_{id} values were obtained from the slope of the linear portions of the curve of different initial concentrations and shown in Table 4. The coefficient of regression values for
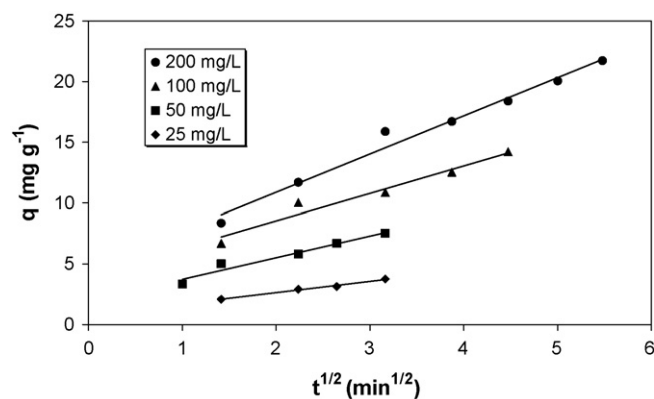

Fig. 13. Intraparticle diffusion plot for the sorption at different initial mercury concentrations (conditions: sorbent dosage = 2 g (500 mL)$^{-1}$; stirring speed = 400 rpm; T = 20 °C; pH 5).

Table 4
Intraparticle diffusion parameters for the sorption of mercury at various initial concentrations (sorbent dosage = 4 g L^{-1}, T = 20 °C, pH 5).

C_0 (mg L^{-1})	k_{id} (mg g^{-1} min$^{-1/2}$)	c (mg g^{-1})	R^2
25	0.93	0.78	0.9878
50	1.78	1.95	0.9550
100	2.25	4.03	0.9579
200	3.15	4.60	0.9817

this diffusion model were between 0.9550 and 0.9878, suggesting that the sorption of mercury by eucalyptus bark can be followed by an intraparticle diffusion model. It was found that the rate constant increased with increasing metal concentration. It can be also observed that the plots did not pass through the origin (the plots have intercepts in the range 0.78–4.60 mg g^{-1}); this is indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic mechanisms may control the rate of sorption, all of which may be operating simultaneously. The values of the intercept also give an idea about the boundary layer thickness: the larger the intercept, the greater is the boundary layer effect. Namely, any increase in the value of c indicates the abundance of solute in the boundary layer. As seen in Table 4, the value of c increases with increasing concentration.

3.5. Sorbent characterization

Microscopy observations showed that the eucalyptus bark surface is quite rough, providing a large exposed surface area for the sorption of mercury ions (Fig. 14). Physicochemical characteristics of eucalyptus bark are given in our previous paper [12].
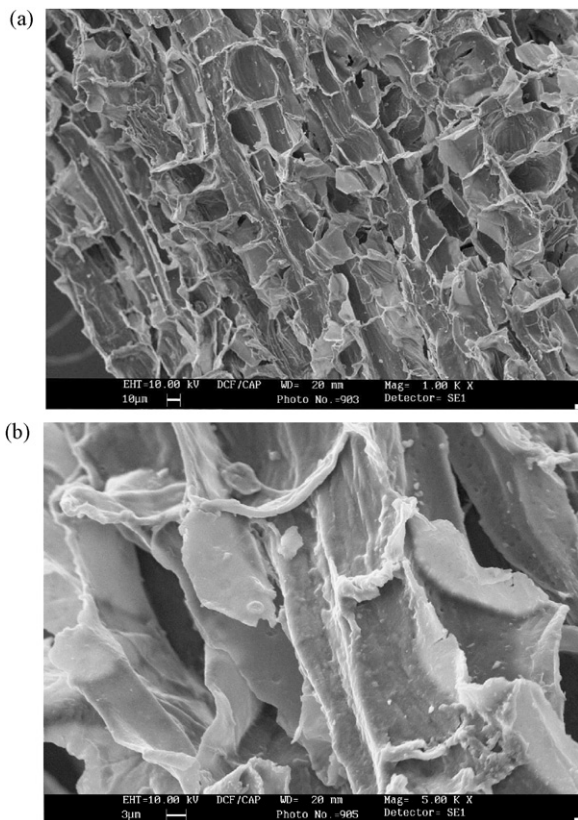
Fig. 14. SEM micrographs of eucalyptus bark surface: (a) magnification 1000×, (b) magnification 5000×.

4. Conclusions

The present work shows that eucalyptus bark can be used as a sorbent for the removal of Hg(II) ions from aqueous media. Experimental data indicated that the sorption capacity was dependent on operating variables such as sorbent dosage, ionic strength, stirring speed, temperature, solution pH, contact time, and initial metal concentration. The process was strongly pH-dependent. Kinetic measurements showed that the sorption process was uniform and rapid. Modeling of sorption kinetics showed good agreement of experimental data with the pseudo-second-order kinetic equation for different initial metal concentrations. The Langmuir model yielded a much better fit than the Freundlich model. The maximum sorption capacity was determined to be 33.11, 33.22, and 34.60 mg g^{-1} at 20, 30, and 40 °C, respectively. The R_L values showed that eucalyptus bark was favorable for the sorption of mercury. The negative values of free energy change and positive value of enthalpy change indicated that the Hg(II) sorption process is spontaneous and endothermic.

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